

FORM PTO-1390 (REV 10-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 205,188
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/857250
INTERNATIONAL APPLICATION NO. PCT/EP99/09367	INTERNATIONAL FILING DATE 2 December 1999	PRIORITY DATE CLAIMED 2 December 1998	
TITLE OF INVENTION DEVICE AND METHOD TO CONTROL STEEL PICKLING PROCESSES			
APPLICANT(S) FOR DO/EO/US GIORDANI ET AL.			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).</p> <p>4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p style="margin-left: 20px;">b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p style="margin-left: 20px;">d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). UNEXECUTED</p> <p>10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p>			
Items 11 to 16 below concern document(s) or information included:			
11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.			
12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.			
13. <input checked="" type="checkbox"/> A FIRST preliminary amendment.			
<input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.			
14. <input type="checkbox"/> A substitute specification.			
15. <input type="checkbox"/> A change of power of attorney and/or address letter.			
16. <input checked="" type="checkbox"/> Other items or information:			
<p>1. International Search Report;</p> <p>2. IPEA Report with amended claims annexed; Pages 2 and 4 have been amended from the specification of the PCT Published Application; they are listed as page 2 and 2a page 4 and 4a in the IPEA Report <i>as amended sheets (annexed)</i>.</p> <p>3. PCT/IB/308;</p> <p>4. PCT/IB/332.</p>			

JC18 Rec'd PCT/PTO 3 0 MAY 2001

U.S. APPLICATION NO. 097857250	INTERNATIONAL APPLICATION NO. PCT/EP99/09367	ATTORNEY'S DOCKET NUMBER 205,188
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17. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

CALCULATIONS PTO USE ONLY

\$860.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	54 - 20 =	34	X \$18.00	\$ 612.00	
Independent claims	2 - 3 =	0	X \$80.00	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$	

TOTAL OF ABOVE CALCULATIONS =

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.

SUBTOTAL =

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).

TOTAL NATIONAL FEE =

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

TOTAL FEES ENCLOSED = \$1,472.00

Amount to be refunded:	\$
charged:	\$

- a. ☒ A check in the amount of \$ 1,472.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01-0035. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

ABELMAN, FRAYNE & SCHWAB
150 E. 42nd Street
New York, New York 10017
(212) 949-9022

SIGNATURE:

JAY S. CINAMON, ESQ.

NAME

24,156

REGISTRATION NUMBER

09/857250

USPTO 30 MAY 2001

PATENT DOCKET 205,188

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: GIORDANI ET AL. EXAMINER:
SERIAL NO.: Not Yet Assigned ART UNIT.:
FILED: Herewith
TITLE: DEVICE AND METHOD
TO CONTROL STEEL
PICKLING PROCESSES

May 30, 2001

PRE-EXAMINATION AMENDMENT

Hon. Commissioner of
Patents and Trademarks
Washington, D.C. 20231

SIR:

STATEMENT OF FILING BY EXPRESS MAIL 37 C.F.R. § 1.10

This correspondence is being deposited with the United States Postal Service on May 30, 2001 in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EK 908 124 694 US addressed to the Honorable Commissioner for Patents, Washington, D.C. 20231.

Please amend the application filed on even date herewith, prior to proceeding with its examination.

IN THE CLAIMS

Please amend claims 7, 21, 33, and 38 as follows:

7. (Amended) Control device according to claim 1, characterised in that one of the analysis devices (A1, respectively A2) measures the concentrations in the pickling bath of sulphuric and of hydrofluoric acids and adds sulphuric and hydrofluoric acids to the pickling bath in order to restore relevant given concentration levels, while the other analysis device (A2, respectively A1) measures the concentrations in the pickling bath of the iron ions and adds oxidant agent to the pickling bath to restore the given value of trivalent iron ion concentration and/or the ratio between trivalent and bivalent iron ions.

21. (Amended) Control device according to claim 8, characterised in that the analysis device (A) also comprises means for chemically washing and water rinsing the analysis vessel (CA), the measure electrode (E) and the porous septum (SP) of the saline bridge, respectively the analysis vessel (CA) and the conductivity measure cell (CC), said means comprising at least slits (F) placed along the upper edge of the vessel (CA) and a nozzle (U) apt to direct a water flow on the extremity of the measure electrode (E) and on the porous septum (SP), respectively on the conductivity measure cell (CC).

33. (Amended) Method according to claim 29, characterised in that said volume

of water is filled into the analysis vessel (CA) through an overflow tube incorporated into the analysis vessel (CA).

38. (Amended) Method according to claim 36, characterised in that the chemical washing comprises at least the following operations:

filling with water the analysis vessel (CA) through slits (F) placed around the upper edge of the analysis vessel (CA) up to have the tip of said means to make potentiometric measures and the conductivity measure cell immersed;

picking up from a tank the amount of the product necessary to obtain the chemical washing solution and sending the latter into said analysis vessel (CA);

after a given period of time, emptying the analysis vessel (CA) and rinsing it with water to eliminate any trace of the washing chemical solution.

Please add new claims 49-54, as follows:

--49. Control device according to claim 3, characterised in that one of the analysis devices (A1, respectively A2) measures the concentrations in the pickling bath of sulphuric and of hydrofluoric acids and adds sulphuric and hydrofluoric acids to the pickling bath in order to restore relevant given concentration levels, while the other analysis device (A2, respectively A1) measures the concentrations in the pickling bath of the iron ions and adds oxidant agent to the pickling bath to restore the given value of trivalent iron ion concentration and/or the ratio between trivalent and bivalent iron ions.--

--50. Control device according to claim 6, characterised in that one of the analysis devices (A1, respectively A2) measures the concentrations in the pickling bath of sulphuric and of hydrofluoric acids and adds sulphuric and hydrofluoric acids to the pickling bath in order to

restore relevant given concentration levels, while the other analysis device (A2, respectively A1) measures the concentrations in the pickling bath of the iron ions and adds oxidant agent to the pickling bath to restore the given value of trivalent iron ion concentration and/or the ratio between trivalent and bivalent iron ions.--

--51. Control device according to claim 14, characterised in that the analysis device (A) also comprises means for chemically washing and water rinsing the analysis vessel (CA), the measure electrode (E) and the porous septum (SP) of the saline bridge, respectively the analysis vessel (CA) and the conductivity measure cell (CC), said means comprising at least slits (F) placed along the upper edge of the vessel (CA) and a nozzle (U) apt to direct a water flow on the extremity of the measure electrode (E) and on the porous septum (SP), respectively on the conductivity measure cell (CC).--

--52. Control device according to claim 17, characterised in that the analysis device (A) also comprises means for chemically washing and water rinsing the analysis vessel (CA), the measure electrode (E) and the porous septum (SP) of the saline bridge, respectively the analysis vessel (CA) and the conductivity measure cell (CC), said means comprising at least slits (F) placed along the upper edge of the vessel (CA) and a nozzle (U) apt to direct a water flow on the extremity of the measure electrode (E) and on the porous septum (SP), respectively on the conductivity measure cell (CC).--

--53. Method according to claim 31, characterised in that said volume of water is filled into the analysis vessel (CA) through an overflow tube incorporated into the analysis vessel (CA).--

--54. Method according to claim 37, characterised in that the chemical washing

comprises at least the following operations:

filling with water the analysis vessel (CA) through slits (F) placed around the upper edge of the analysis vessel (CA) up to have the tip of said means to make potentiometric measures and the conductivity measure cell immersed;

picking up from a tank the amount of the product necessary to obtain the chemical washing solution and sending the latter into said analysis vessel (CA);

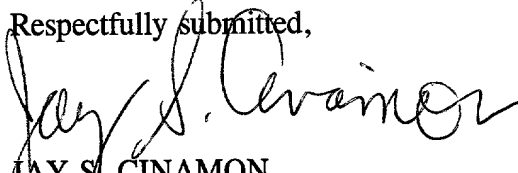
after a given period of time, emptying the analysis vessel (CA) and rinsing it with water to eliminate any trace of the washing chemical solution.--

REMARKS

It is respectfully requested that the examination of this application proceed on the basis of the amendatory action taken herein and that this amendment be entered prior to calculating the filing fee and according the application a filing date.

Please note that attached is a Marked-Up Version Showing Changes Made by this Amendment to the amended claims under Chapter II as attached to the International Preliminary Examination Report.

Respectfully submitted,


JAY S. CINAMON
Registration No. 24,156
Attorney for Applicants

ABELMAN FRAYNE & SCHWAB
150 East 42nd Street
New York, New York 10017-5612
Tel. (212) 949-9022
Fax (212) 949-9190
notarbar\53001gio.px

Docket No. 205,188

MARKED-UP VERSION SHOWING CHANGES MADE BY AMENDMENT

Claims 7, 21, 33 and 38 have been amended as follows:

7. (Amended) Control device according to claim 1, ~~3 and 6~~, characterised in that one of the analysis devices (A1, respectively A2) measures the concentrations in the pickling bath of sulphuric and of hydrofluoric acids and adds sulphuric and hydrofluoric acids to the pickling bath in order to restore relevant given concentration levels, while the other analysis device (A2, respectively A1) measures the concentrations in the pickling bath of the iron ions and adds oxidant agent to the pickling bath to restore the given value of trivalent iron ion concentration and/or the ratio between trivalent and bivalent iron ions.

21. (Amended) Control device according to claim 8, ~~14 and 17~~, characterised in that the analysis device (A) also comprises means for chemically washing and water rinsing the analysis vessel (CA), the measure electrode (E) and the porous septum (SP) of the saline bridge, respectively the analysis vessel (CA) and the conductivity measure cell (CC), said means comprising at least slits (F) placed along the upper edge of the vessel (CA) and a nozzle (U) apt to direct a water flow on the extremity of the measure electrode (E) and on the porous septum (SP), respectively on the conductivity measure cell (CC).

33. (Amended) Method according to claim 29 ~~or 31~~, characterised in that said volume of water is filled into the analysis vessel (CA) through an overflow tube incorporated into the analysis vessel (CA).

38. (Amended) Method according to claim 36 ~~and 37~~, characterised in that the chemical washing comprises at least the following operations:

filling with water the analysis vessel (CA) through slits (F) placed around the upper edge of the analysis vessel (CA) up to have the tip of said means to make potentiometric measures and the conductivity measure cell immersed;

picking up from a tank the amount of the product necessary to obtain the chemical washing solution and sending the latter into said analysis vessel (CA);

after a given period of time, emptying the analysis vessel (CA) and rinsing it with water to eliminate any trace of the washing chemical solution.

DEVICE AND METHOD TO CONTROL STEEL PICKLING PROCESSES**Field of invention**

The invention consists in a device and in a method to control pickling processes for carbon steels, austenitic, ferritic and martensitic stainless steels, duplex steels and special alloys, in which said device automatically manages sampling of pickling baths and analysing of said samples in order to define (according to specific conductivity and potentiometric methodologies) critic process parameters and to restore desired concentrations of necessary chemicals in the pickling tanks. The invention also permits to manage pickling conditions specific for the type of steel under treatment through definition of remotely activable operative procedures automatically recalling and realising the most apt operating conditions for pickling of the specific kind of material under treatment.

State of the art

In the rolling, drawing, extrusion, heat treatment of steel products (such as plates, strips, tubes, rods) oxide layers are formed on the surface thereof which must be removed both to get proper final appearance as well as passivity and anticorrosive properties for the final product, and to allow further working.

Said superficial oxide layers are usually eliminated by a chemical treatment (pickling) based on exposition of the metallic material to the action of one or more acid baths containing inorganic mineral acids (sulphuric, hydrochloric, nitric, hydrofluoric) alone or mixed with one another, at proper dilution and temperature, followed by at least one final rinsing in water.

For stainless steels, the usual pickling processes (either by immersion, spraying or turbulence) require a mixture of nitric and hydrofluoric acids; such processes entrain very serious ecological problems due to emission of the reaction by-products (extremely toxic nitrogen oxides) into the atmosphere as well as of great quantities of nitrates into waste water.

Hence, during the recent past a number of alternative "ecological" processes have been devised characterised by the elimination of nitric acid.

Among such processes, particularly effective at the industrial scale are those utilising mixtures of sulphuric or hydrochloric acid, hydrofluoric acid and ferric ions, in which the proper concentration of such ions into the pickling bath is maintained

through addition of hydrogen dioxide. Some of such processes are described in Italian patents 1,245,594 and 1.255.655 (corresponding to US-A-5 345 383) and in European patent application EP-A-0 769 575.

In the traditional pickling technology, the management of the process usually includes an occasional control of the pickling bath through manual titration of the acidity or measure of the conductivity of the solution and of its iron content (or of total metals, through measurement of bath density); it is also possible to measure the content in hydrofluoric acid by means of a specific ion selective electrode.

Some of these techniques have been utilised in the automation of single operations in nitric acid based pickling processes of stainless steels.

US patent 4,060,717 (LECO Corp.) discloses the use of ions selective electrodes for fluorine and hydrogen ions to measure the concentration of nitric acid (or other strong acid) and of hydrofluoric acid in pickling baths containing nitric and hydrofluoric acids; the electric voltage data gathered by a control circuit are elaborated by a microprocessor to calculate the concentration of the two acids and to adjust relevant concentrations.

JP patent 55040908 (NIPPON Steel Corp.) discloses the determination of the hydrofluoric acid and of another strong acid (nitric, hydrochloric, sulphuric) through the determination with ion selective electrodes of the relevant anions after passing the solution through ion exchange membranes, in order to adjust the acids concentration.

US patent 5,286,368 (FOXBORO Corp.) measures the concentration of hydrofluoric acid in a mixture of nitric and hydrofluoric acids through the complexing ability of trivalent iron ions towards the fluorine ions, permitting to determine the concentration of the acids in the mixture.

JP patent 072944509 (KAWASAKI Steel Corp.) measures the concentrations of free hydrofluoric and nitric acids and that of iron ion in a pickling solution by measuring the concentration of iron ion by an iron salicylate complex absorptiometric method, the concentration of free hydrofluoric acid by an iron acetylacetone complex fading absorptiometric method and the total concentration of free acids by neutralising titration method, the concentration of free nitric acid being measured by subtracting the concentration of free hydrofluoric acid from the

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total concentration of free acids.

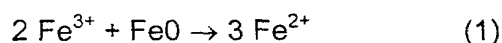
JP patent 081660003 (MITSUBISHI Heavy Ind. Ltd.) refers to a method for continuously measuring the iron ion concentration in a pickling solution.

The continuous automatic management of such pickling processes based on nitric acid, though better than an occasional manual or automatic control performed, for instance, a few times per day, is not essential for the process in terms of quality of treated material, because of the functional characteristics of such baths; particularly, in the pickling of stainless steels, such baths usually have high nitric acid concentrations (about 12-15%) and hydrofluoric acid concentration of about 2-5%. The high nitric acid concentration ensures at the same time both high acidity and almost constant oxidising power, making it possible to manage the process

through occasional additions of chemicals. Moreover, the determination of acid concentration is sufficient to have an adequate control of the pickling ability of the bath.

On the contrary, the nitric acid free pickling systems, such as those previously cited, found the oxidising properties of the system on the measure of the ferric ions (Fe^{3+}) concentration, or better on the control of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio.

In this case, because of the pickling reaction (1)

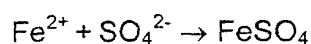
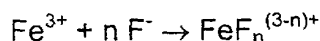


in a continuous process for the production of stainless steel strips or in automatic, high productivity plants for rod pickling, the trivalent iron ions concentration, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio and hence the oxidising capacity of the solution tend to quickly diminish, continuously and drastically modifying the bath behaviour.

The optimal conditions must be, therefore, continuously adjusted by means of oxidising agents, such as hydrogen peroxide.

Moreover, the variation of the trivalent iron concentration indirectly influences also the concentration of the free acids present into the bath.

For instance, in a pickling system based on sulphuric acid, hydrofluoric acid and ferric salts mixtures, this influence is linked to the following preferred equilibria:



Hence, during the oxidation/reduction reaction of the couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ liberation of respectively sulphuric acid and of hydrofluoric acid will occur from relevant complex salts, thus modifying the bath composition.

A process control through occasional analytic measures, followed by large additions of chemicals to restore the best pickling conditions, causes, therefore, too ample variations of the bath parameters with adverse consequences on the product quality and on the process costs.

On the other hand, frequent manual controls and relevant composition adjustments are time consuming and costly, since this requires a large amount of personnel to ensure a satisfactory control frequency (e.g. a control per hour).

The criticality of nitric acid free pickling processes is obviously linked to the total iron amount dissolved per time unit, to the number of pickling tanks to be controlled, to

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the number of materials requiring different operative conditions and to the practical capability to ask for frequent manual additions of acids into the tanks.

The management of pickling processes for stainless steels such as those previously cited for continuous pickling plants of stainless steel strips or for high productivity automatic plants for rod processing, proved to be critic for the quality of the final product; it can also be non economic without the use of an automatic system for sampling, controlling and dosing of the reactants.

The control device and the method according to the present invention require the utilisation of specific skilfulness and analytical methods for a proper management of such processes.

Summary of the invention.

It is an object of present invention a control device for nitric acid free pickling baths comprising means to take a sample of the bath to be analysed; means to analyse said sample in order to measure a number of parameters according to specific conductivity methodologies (to find out the concentration of hydrofluoric acid, of the sulphuric acid or of another inorganic strong acid) and potentiometric methodologies (to find out the concentrations of trivalent and bivalent iron) as well as to measure the redox potential value of said sample and its temperature; restoring means, apt to calculate, according to the above measured values, the quantity of correction chemicals (preferably hydrofluoric acid, sulphuric acid and an oxidising agent) to be added to the pickling bath in order to restore at the desired level the value of said parameters and to actuate at least a device to add into said pickling bath said quantities of correction chemicals.

Preferably, the measured parameters are the concentration of sulphuric acid, that of hydrofluoric acid and those of bivalent and trivalent iron ions.

It is a further object of present invention a control method for controlling nitric acid free pickling baths, which comprises at least the steps of:

- taking a sample of a pickling bath;
- measuring the concentration in said sample of a pickling bath of the acids, of the bivalent iron and of the trivalent iron;
- measuring the redox potential and the temperature of said sample of a pickling bath;

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- restoring at preset levels the values of said measured concentrations in said pickling bath by adding calculated quantity of correction chemicals to the pickling bath.

List of Figures

- 5 The invention will now be described with reference to a non limiting embodiment shown in the enclosed figures where:

Fig. 1 schematically shows a plant comprising an analysis device according to the invention;

Fig. 2 shows a simplified scheme of an analysis device according to the invention;

- 10 Fig. 3 schematically shows the analysis vessel CA of Fig. 2, comprising a conductivity measuring system and a preferred embodiment of the rinsing means of the vessel itself and of the measure electrode;

Fig. 4 schematically shows the analysis vessel CA of Fig. 2, comprising a potentiometric measuring system and a preferred embodiment of the rinsing means of the vessel itself and of the measure electrode.

In the enclosed Figures, corresponding elements will be identified with same reference.

Detailed description of the invention

Fig. 1 schematically shows a plant comprising an analysis device according to the invention, comprising:

- a plurality of pickling tanks V (V1, ..., Vn);
- an analysis device A (later on described with reference to the simplified scheme of Fig. 2) which, in the herein described embodiment, includes a couple of analysis devices (A1, A2) simultaneously working on different parameters;
- a plurality of reservoirs S (S1, S2, S3) each containing a solution at a given concentration of one of the correction chemicals (a strong mineral acid, preferably sulphuric acid, hydrofluoric acid and an oxidising agent, preferably but not necessarily hydrogen peroxide) to be added into one of the tanks V;
- a plurality of permanent recycling piping, connecting tanks V to the sampling inputs I (Fig. 2) of the analysis device A;
- a plurality of piping to feed the correction chemicals, connecting reservoirs S to tanks V;
- addition means enabling the analysis device A to control the addition into tanks V of correction chemicals contained in reservoirs S.

For simplicity, in Fig. 1 components not interesting for the present description, such as valves, pumps, actuators, filtering and rinsing means, known per se, as well as other, if any, circuitry components are omitted.

The analysis device A comprises (Fig. 2) means to pick up from a vessel V a sample of the pickling bath; means to analyse it to measure, according to specific conductivity and potentiometric methodologies, the preset parameters (the strong mineral acid, for instance sulphuric acid, and the hydrofluoric acid concentrations, as well as the ones of trivalent and bivalent iron), the redox potential and the temperature of said diluted sample; means to calculate the amounts of correction

chemicals to be sent from reservoirs S to tanks V to adjust said parameters and means to actuate the devices at the output of reservoirs S to send into the pickling bath the calculated amounts of said correction chemicals.

Hereinafter, "sulphuric acid" will mean any strong mineral acid.

5 Since the time necessary for measuring the concentration of sulphuric and hydrofluoric acids is shorter than that necessary for the measure of iron ions concentration (just some minutes vs about 30 minutes), the analysis devices (A1, A2) are preferably divided, each one being specialised in only one of said analysis (measure of sulphuric acid and of hydrofluoric acid, respectively of iron ions
10 concentrations).

The analysis devices (A1, A2) can be managed by a logic unit of higher level, not shown in the figures, which can be placed "in loco" or in a remote site, connected to the analysis devices (A1, A2) through bi-directional transmission means, known per se.

15 Alternatively, said analysis devices (A1, A2) can be of the same model and comprise the analytical means apt to measure the concentration both of the acids (sulphuric and hydrofluoric) and of the iron ions.

In such a case, the device according to the invention could also work in case of malfunction of one of the analysis devices (A1, A2).

20 Fig. 2 shows a simplified scheme of an analysis device A (A1, A2) of Fig. 1, comprising in combination relationship:

- a sampling module C, the sampling inputs of which I (I1, ..., In) are in sequence connected to the permanent recycling piping among the pickling tanks V (V1, ..., Vn; Fig. 1) and the analysis device A; at least a reservoir (not shown), in which the bath sample to be analysed is loaded, is provided inside
25 the sampling module C;
- a reagent storage DR, containing the chemicals for the analyses;
- dosing means D (D1, D2) apt to draw the amounts of chemicals necessary to the analyses and to transfer the same into the analysis vessel CA, part of the
30 dosing means D being apt to draw with low accuracy (from about 2 to about 5%) high quantities of chemicals, the remaining dosing means being apt to draw with high accuracy (about 0,1%) small quantities of chemicals; in Fig. 2

the dosing means D with low and high accuracy are respectively grouped in two different functional units (D1, D2).;

- an analysis vessel CA, containing the measure electrodes (generically named EM in Fig. 2), receiving from sampling module C the bath sample to be analysed, from dosing means D the chemicals necessary for the analysis and from a reservoir W (not shown) the water (preferably having a conductivity lesser than 100 microsiemens) necessary to dilute said sample to a desired dilution ratio; in Fig. 2 further elements (such as stirrers) present in analysis vessel CA are omitted, not being part of present invention;
- a logic unit UL, controlling and managing the analysis procedures, acquiring and elaborating the information from measure electrodes EM and actuating means to send into the pickling bath the solutions of the correction chemicals contained in the reservoirs S (Fig. 1).

In a preferred but not limiting embodiment the dosing means of functional unit D1 are peristaltic pumps with constant delivery, while the dosing means of functional unit D2 are syringes in antacid material (e.g. PES) operated by an electric stepping motor.

Again in a preferred embodiment, the analysis device A also comprises means (hereinafter described with reference to Figures 3 and 4) permitting to rinse the analysis vessel CA and the measure electrodes EM after each measure with water and after a given number of measures with a chemical solution (preferably but not necessarily 10-20% hydrochloric acid), thus permitting to keep in optimal conditions the measure electrodes EM, to have reliable analytical data, to reduce to a minimum the maintenance interventions and to highly enhance the electrodes life.

To ensure a constant quality of the final product, each type or family of materials to be pickled must be treated according to standard and characteristic parameters (hydrofluoric and sulphuric acids concentration, trivalent and bivalent iron ions concentration, ratio between trivalent and bivalent iron ions, hydrogen peroxide concentration, temperature of the sample to be analysed, and so on); in a preferred embodiment of the invention, the parameters characterising each working step as well as those concerning the operation of the analysis device A,

which all permit to perform different analyses on pickling baths relating to the specific working step, are grouped into operating procedures biuniquely correlated with the material itself and stored in the logic unit UL, which are when necessary recalled according to the material to be pickled.

5 Preferably but not necessarily, an operating procedure comprises at least the following information:

- the order and the kind of the analyses to be performed;
- the prefixed values of the parameters for the pickling bath;
- the magnitude of the admissible deviations with respect to the prefixed values,
10 beyond which the logic unit UL actuates said means to send into the pickling bath the solutions of the correction chemicals contained in reservoirs S,
- the dilution ratios with water in the analysis vessel CA of the pickling bath sample to be analysed.

The proper operation of the analysis device A can be advantageously checked periodically and automatically; to this end, in a preferred embodiment of the
15 present invention a further operative autocalibration procedure is stored in the logic unit UL which activates after a given number of analyses and comprises the functional steps of drawing from a container (preferably but not necessarily located in the reagent storage DR) a fixed amount of a standard solution having a known
20 composition, of transferring it into the analysis vessel CA, of analysing it, of comparing the obtained analytical results with the known composition and of activating alarm signals if the deviation between obtained analytical results and known concentrations is larger than a desired value.

According to an embodiment of present invention, not shown in the figures, the
25 logic unit UL can be connected to a central operative post and/or to a logic unit of higher level, by which it can be controlled and managed; as above said, this logic unit of higher level can be placed "in situ" or be remote.

In particular, at each change of working activity, the central post operator can modify the operative procedure performed by one or more of the logic units UL,
30 activating the one pertaining to the activity to be initiated; the operator can also recall from one or more of the logic units UL an operating procedure, modify it and have it to be performed by the logic units UL and/or inputting a new operative

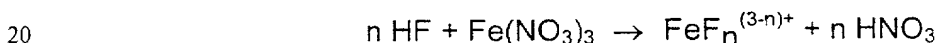
procedure storing it in the logic units UL.

The analytical methods, which are utilised in the analysis of the pickling baths, will now be described to better understand the described details, which are part of present invention.

- 5 a) Conductivity determination of hydrofluoric acid and of sulphuric acid (or of other acid strong with respect to hydrofluoric acid).

This determination is based on the principle that, in an aqueous solution formed by a mixture of a weak acid such as hydrofluoric acid and of a stronger acid such as sulphuric acid, the solution conductivity is practically equivalent to the one of the
10 strong acid at the same concentration; the method also exploits (in a stage subsequent to a first conductivity measure on a bath sample duly diluted to measure the sulphuric acid concentration) the high affinity of hydrofluoric acid for a metal cation present in the solution as a salt of known concentration. The salt anion most preferably come from a strong acid (e.g. nitric or hydrochloric acid) so
15 that the reaction forming fluorocomplexes of the metal cation and hydrofluoric acid will generate a significant increase of conductivity due to the formation of an equivalent amount of fully dissociated strong acid, measured by a second conductivity measure.

For instance:



Such conductivity increase is, therefore, proportional to the concentration of hydrofluoric acid which, after a proper calibration, can be quantitatively measured.

Such salts can be, for instance, ferric nitrate, ferric chloride, aluminium nitrate, aluminium chloride; in a preferred embodiment of the invention a solution of ferric
25 nitrate*9H₂O is utilised, at a concentration of 750 g/l.

To ensure a sufficiently linear dependence of conductivity from the variation of acids concentration, the sample dilution must be attentively evaluated as a function of the concentration of the acids present in the bath to be analysed; as a non-limiting example, for sulphuric acid concentrations up to 200 g/l and for
30 hydrofluoric acid concentrations up to 60 g/l, dilution ratios from 1:100 to 5:100, and preferably 4:100, are deemed to be acceptable.

Another variable essential for the obtainment of reliable results (which must be

managed by the logic unit UL of the analysis device A) is the sample temperature after dilution with water; in fact, in the industry the water temperature can have considerable variations (usually between +5 and +40° C) according to the weather, to the water source and to the holding time in reservoir W.

5 It is apparent that a conductivity measure is greatly influenced by the temperature, and usually such a problem is overcome by means of an automatic compensation system incorporated into the measure device; in the present case, the automatic compensation can correctly adjust only the effect on the first conductivity measure (determination of the sulphuric acid concentration) but not on the second one
10 (determination of the hydrofluoric acid concentration) performed after addition of ferric nitrate as the solution composition is changed and its dependence from the temperature is, in fact, different before and after the ferric nitrate addition.

This critical problem is solved with an analysis device A according to the invention, in which the logic unit UL takes into account the conductivity variation due to the
15 addition of a volume v_3 of the ferric nitrate solution, depending on the sample temperature.

The amount of ferric nitrate utilised during the titration must be such to ensure a full complexing of the hydrofluoric acid; in the considered system, for hydrofluoric acid concentration less than 60 g/l the ratio between the volume v_3 of a solution of
20 ferric nitrate*9H₂O at 750 g/l and the volume v_1 of the bath sample must be higher than 0,5 and preferably 1.

As a non limiting example the following operating procedure is given along with relevant computations for a sample dilution of 4:100 in volume:

- filling of the analysis vessel CA, by means of dosing means D2, with a given
25 water volume v_2 , having a conductivity of less than 100 microsiemens to obtain a dilution ratio of 4:100;
- picking up from the sampling module C (by means of dosing means D2) of a given volume v_1 of the pickling bath sample to be analysed;
- start stirring the solution;
- 30 • first conductivity measure (L_1);
- addition of a given volume $v_3 = v_1$ of a solution of ferric nitrate*9H₂O at 750 g/l;

- stirring of the solution and measuring of its temperature T;
- second conductivity measure (L_2).

The logic unit UL acquires the data L_1 , L_2 , T and automatically find the concentration of the acids through the following calculations:

- 5 • sulphuric acid concentration (g/l): $a \cdot L_1^2 + b \cdot L_1 - c$
- hydrofluoric acid concentration (g/l): $a_1 \cdot \delta^2 + b_1 \cdot \delta - c_1$

where:

a, b, c, a_1 , b_1 , c_1 are coefficients of the quadratic equations;

$$\delta = L_2 - L_1 - \phi;$$

$$10 \quad \phi = c_2 + (c_3 \cdot T);$$

c_2 , c_3 are constants depending on the quantity of ferric nitrate*9H₂O added to the diluted sample before the second conductivity measure.

In this example:

$$a = 0,0066; b = 5,015; c = 6,98$$

$$15 \quad a_1 = 0,0120; b_1 = 2,881; c_1 = 3,81;$$

$$c_2 = 9,632; c_3 = 0,297.$$

Fig. 3 shows the characteristics of the conductivity cell CC, which specific form allows to minimise the negative effects due to the high viscosity of the solution and to facilitate the rinsing of the measure platinum plaques.

20 Said conductivity cell CC comprises a hollow body B, in glass and having a substantially cylindrical shape, containing two blackened platinum plaques EL; at the lower and upper parts of the hollow body B there are holes (F1, F2) letting the sample to be analysed to circulate inside the hollow body B.

Preferably, the hollow body B has a diameter of about 20 mm (and anyhow comprised between about 17 and 23 mm) and a height of about 40 mm (and anyhow comprised between about 35 and 45 mm); the EL plaques dimensions are about 10 x 5 mm (and anyhow between about 8 x 12 mm and about 3 x 7mm), the distance from one another being about 15 mm (and anyhow between about 12 and 18 mm).

30 To avoid polarisation of electrodes EL, the measure electric circuit (not shown) connected to the conductivity cell CC must work at high frequency (between 25 and 40 kHz).

b) Determination of bivalent iron

The bivalent iron determination can be made through potentiometric analysis, by potassium permanganate titration according to the classic methodology.

The operative sequence requires:

- 5 • pouring into the analysis vessel CA a given water volume v_2 , through the overflow pipe TP, to obtain a dilution ratio $\geq 1:50$;
- picking up from the sampling module C (by means of dosing means D2) a given volume v_1 of the pickling bath sample to be analysed, and addition of said sample into the analysis vessel CA;
- 10 • acidification of the diluted pickling bath sample by means of addition into the analysis vessel CA (by means of dosing means D1) of a given non-critical amount of a solution of a strong acid, e.g. a sulphuric acid solution 1:1 bw;
- potentiometric titration, having a preset final point or with an automatic search of the final point with a 0,1N potassium permanganate solution added into analysis vessel CA by means of dosing means D2;
- 15 • emptying and rinsing analysis vessel CA.

c) Determination of trivalent iron

The trivalent iron is measured by iodometric titration, utilising however some specific attention to permit the use of an automatic device and the obtention of reliable and reproducible results.

Said determination requires the following operating sequence:

- pouring into the analysis vessel CA a given water volume v_2 , through the overflow pipe TP, to obtain a dilution ratio $\geq 1:50$;
- 25 • picking up from the sampling module C (by means of dosing means D2) a given volume v_1 of the pickling bath sample to be analysed, and addition of said sample into analysis vessel CA;
- start of stirring;
- addition into analysis vessel CA (by means of dosing means D1) of a given non-critical volume of a lanthanum nitrate solution having a known concentration;
- 30 • waiting for 30 s without stirring;
- addition into analysis vessel CA (by means of dosing means D1) of a given

non-critical volume of a hydrochloric acid solution at 1:1 vol;

- addition into analysis vessel CA (by means of dosing means D1) of a given non-critical volume of a potassium iodide solution, at a concentration for instance of 1 kg/l;
- 5 • waiting for 5 min without stirring;
- start of solution stirring;
- potentiometric titration with 0,1N sodium thiosulphate (added by means of dosing means D2) of the iodine liberated by the reaction of trivalent iron with potassium iodide;
- 10 • emptying and water rinsing of analysis vessel CA.

For this automatic analysis, a most prominent aspect is the use of lanthanum nitrate; in fact, the addition of a salt including a cation able to complex the fluorine ion linked to the iron ion is essential for the quantitative analysis of the ferric ion through iodometric analysis.

15 This analysis can be manually performed utilising a solution of calcium chloride; however it was proved that calcium chloride cannot be utilised for the automatic titration of trivalent iron, because of the subsequent precipitation of calcium fluoride and of calcium sulphate, which tend to continuously foul the electrodes in analysis vessel CA, giving rise to significant errors and complex upkeep. On the
20 contrary, it was found that lanthanum salts can quantitatively release the ferric ion, generating powdery and non-sticking lanthanum fluoride precipitates, thus permitting the automatic management of the process with high reliability and very limited upkeep.

This same result can also be achieved by adding to the system a complexing
25 agent for the iron ion, which however can quantitatively release it during the subsequent reaction with potassium iodide; complexing agents such as EDTA can be fit for this purpose.

The potentiometric system, schematically illustrated in Fig. 4, comprises a measure electrode E (inert to the working environment) immersed in analysis
30 vessel CA and a reference electrode R (preferably in glass, of the type Ag/AgCl) positioned outside said analysis vessel CA and in contact with the solution under measurement through a saline bridge, comprising an electrolyte (contained in a

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tank SR) which is made to continuously pass through a porous septum SP placed at an extremity of a small plastic tube T.

The continuous passage of the electrolyte through the septum SP is intended to consent the electric continuity; to avoid the contact between septum SP and the hydrofluoric acid of the pickling bath and to continuously renovate the electrolyte.

In a preferred embodiment, the measure electrode E is made from a body in antacid material bearing at one extremity a platinum plaque P, one of whose surfaces, mirror finished, faces downwards, thus preventing the salts deriving from the reaction products to be deposited on the measuring face of plaque P, fouling it.

Advantageously, to the electrolyte (preferably 3M potassium chloride) can be added a 10% solution of glycerine (of another compatible product having a viscosity at 20°C comprised between 1,15 and 1,45 centipoise, inert with respect to the working environment and functionally equivalent) to enhance the viscosity and reduce the flow speed, thus permitting a better autonomy of the potentiometric system for a given volume of tank SR.

d) Determination of hydrogen peroxide

The determination of the free hydrogen peroxide in nitric acid free pickling processes such as the ones here described, is necessary in the treatment of ferritic and martensitic steels for the control of finishing/passivating baths generally utilised as the last operation before final rinsing; usually said baths comprise sulphuric acid (20-60 g/l), hydrogen peroxide (3-10 g/l) and sometimes hydrofluoric acid.

The analytical methodology and the operative sequence utilised for the determination of the hydrogen peroxide are the same utilised for the determination of bivalent iron in the pickling baths.

e) Determination of the redox potential

The device according to the invention measure, before the determination of bivalent iron, the solution redox potential on the diluted pickling bath sample utilising the potentiometric system already described; the thus obtained value is very near (± 20 mV) to the redox potential measured in the bath before its dilution. The obtained value is compared with a range of values (usually comprised between 200 and 550 mV) stored into the logic unit UL to be utilised as a first

signal of the correct operation of the system: if the measured value is outside of said range, the logic unit UL of the analysis device A stops the analysis procedure and sends an alarm. The calibration of the potentiometric system is made at a given frequency (say, once per week) by redox potential measure on a standard solution of known potential (usually 468 mV).

As already said, the logic unit UL of an analysis device 1 according to present invention, after measuring the desired parameters on the pickling bath sample under analysis, calculates the amount of each of the solutions at known concentration of the correction chemicals (sulphuric acid, hydrofluoric acid and oxidising agent) contained in reservoirs S, said chemicals being opportunely added to the pickling bath to restore the desired composition values and actuates addition means (such as, for instance, dosing pumps or electrovalves) at the output of reservoirs S to send into the pickling bath said calculated amounts of the correction chemicals.

Being known the plant characteristics (volume of tank V, delivery of each adding means, preset concentration values for said correction chemicals, concentration of said chemicals, and so on) to have the correct amount of correction chemicals added to the pickling bath, the logic unit UL must just calculate the actuating period of said addition means.

Studies and experiments of this Applicants did show that, to bring back to the desired values the concentrations in the pickling bath of sulphuric acid, of hydrofluoric acid, of trivalent iron ion and of the oxidising reagent, the logic unit UL must actuate each of the addition means regulating the addition into the pickling bath of the sulphuric acid, hydrofluoric acid and oxidising reagent solutions, for a period of time s (in seconds) given by the following expression:

$$s = K \cdot (v_0 - v_m) \cdot v_b/p$$

in which:

s = actuating time (seconds);

K = factor inversely proportional to the concentration of the correction chemicals (l/g);

v_0 = given concentration for the specific corrective chemical (g/l);

v_m = concentration of said specific corrective chemical resulting from the analysis

(g/l);

V_b = volume of tank V;

p = delivery of the addition means (l/s).

To bring back to the desired value the ratio R between the concentration of trivalent and bivalent iron ions, the logic unit UL calculates the actuating period s1 (in seconds) of the addition means sending into the pickling bath the oxidising reagent solution, by:

- calculating $B_1 = A \cdot R$, in which A is the concentration (g/l) of the bivalent iron ion resulting from the titration with permanganate, R is the desired ratio between the concentration of, respectively, the trivalent and the bivalent iron ions, and B_1 is the theoretical concentration of the trivalent iron ion;
- comparing B_1 with the measured concentration B of the trivalent iron ion (g/l);
- if $B \geq B_1$ (the measured concentration of the trivalent iron ions is greater than that of the bivalent ones) the logic unit UL does not act;
- if $B < B_1$ (the trivalent iron ions concentration is less than the measured one) the logic unit UL calculates the actuating period s1 of the addition means regulating the addition to the pickling bath of the oxidant reagent solution, by means of the formula

$$s1 = K \cdot K_1 \cdot C/p$$

in which:

- s_1 = actuating period (s);
- K factor inversely proportional to the concentration of the correction chemical (i/g),
- K_1 = factor proportional to the tank volume V (l);
- $C = (B_1 - B)/R$ = amount of bivalent iron ion to be oxidised to restore the desired value for iron ion concentration (g/l);
- p = delivery of the addition means (l/s).

Alternatively the bath can be managed in function of the ratio R between trivalent iron and bivalent iron according to the following calculation:

- Calculation of the total iron $T = A + B$

where A is the concentration of Fe^{2+} obtained from the permanganometric analysis and B is the concentration of Fe^{3+} obtained from the iodometric analysis.

- Calculation $R = B/A$
- Compare R (present ratio) with R_1 (pre-fixed ratio)
- If $R > R_1$ the logic unit UL does not make any addition of oxidizing product
- If $R < R_1$ the logic unit UL calculates the actuating period s_1 (in seconds) of the addition means regulating the addition the pickling bath of the oxidizing product solution according to the following formula

$$s_1 = K \cdot K_1 \cdot C/p$$

where

$C = A - [(A+B)/(R_1+1)]$ = amount of bivalent iron to oxidize to restore the present ratio R to the prefixed value R_1

s_1 = actuating period (s)

K = coefficient, inversely proportional to the volume of the tank V (l)

P = delivery of the addition means (l/s).

Fig. 3 schematically shows an exploded view of the analysis vessel CA of Fig. 2, comprising a measure system of conductivity type and a preferred embodiment of the rinsing means of analysis vessel CA and of measure cell CC.

In Fig. 3 it is possible to see:

- the conductivity measure cell CC used for conductivity measure;
- the analysis vessel CA;
- the overflow TP, mobile, the position of which (controlled by the logic unit UL) consents to set the liquid level in the analysis vessel CA, and to empty the same vessel;
- rinsing means (F, U) controlled by the logic unit UL, enabling the rinsing of analysis vessel CA and of the conductivity measure cell CC.

Fig. 4 schematically shows an exploded view of the analysis vessel CA of Fig. 2, comprising a potentiometric measure system as well as a preferred embodiment, similar to the one in Fig. 3, of the rinsing means of analysis vessel CA and of the measure electrodes.

In Fig. 4 can be seen:

- the potentiometric system, comprising the measure electrode E, the reference electrode R, positioned outside of the analysis vessel CA, and the saline bridge which in turn comprises an electrolyte contained in tank SR, continuously

passing through a porous septum SP placed at one extremity of a small plastic tube T;

- the analysis vessel CA;
- the mobile overflow TP, the position of which (controlled by the logic unit UL) consents to set the liquid level in the analysis vessel CA, and to empty the same analysis vessel;
- rinsing means (F, U) controlled by the logic unit UL, enabling the rinsing of analysis vessel CA, of the electrode E extremity and of the porous septum SP.

In the preferred embodiment shown in Figures 3 and 4, such rinsing means comprise a plurality of slits F placed along the upper edge of the analysis vessel CA and a nozzle U apt to rinse with a water spray the extremity of the measure electrode E and the porous septum SP, respectively the conductivity measure cell CC; in Figures 3 and 4, can also be seen the lid CP for the analysis vessel CA and means MS supporting the electrode E, the small tube T of the potentiometric system, the conductivity measure cell CC and the small tubes (not explicitly indicated in Figures 3 and 4) connecting the dosing means D (D1, D2) with the analysis vessel CA; lid CP and supporting means MS will not be described, as known per se and anyhow not pertaining to present invention.

Preferably, the analysis vessel CA, the measure electrode E and the porous septum SP (respectively the analysis vessel CA and the conductivity measure cell CC) are water rinsed after each analysis and washed with a chemical solution after a given number of analyses.

To rinse said components with water after each analysis the logic unit UL performs in sequence the following steps:

- fully emptying analysis vessel CA;
- pouring in said analysis vessel CA a large amount of water through slits F;
- filling with water analysis vessel CA up to have the tip of electrode E and the porous septum SP, respectively the conductivity measure cell CC immersed;
- emptying analysis vessel CA;
- further rinsing the tip of electrode E and the porous septum SP, respectively the conductivity measure cell CC by spraying on them some water through nozzle U;

- emptying analysis vessel CA and preparing it for the subsequent analysis.

To wash after a given number of analyses with a chemical solution (preferably 10-20% hydrochloric acid) the analysis vessel CA, the tip of electrode E and the porous septum SP (respectively the analysis vessel CA and the conductivity measure cell CC), the logic unit UL fills with water analysis vessel CA through slits F up to have the tip of electrode E and the porous septum, respectively the conductivity measure cell CC immersed, picks up from a tank (preferably but non necessarily placed within the reagent's storage DR) an amount of product (preferably hydrochloric acid) necessary for said chemical washing and send it into analysis vessel CA; after a given period of time the logic unit UL empties analysis vessel CA and rinse it with water, to eliminate any trace of the chemical solution.

Moreover, when not working, analysis vessel CA is filled with water through slits F and nozzle U, to avoid any fouling and/or damaging of the electrode E tip, of the porous septum SP, and of the conductivity measure cell CC.

It is possible for an expert to modify and improve, as suggested by ordinary experience and by the natural technical evolution, the device for the control of pickling baths according to present description, still remaining within the scope of present invention.

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CLAIMS

1. Control device for nitric acid free pickling baths characterised in that it comprises means to take a sample of the bath to be analysed; means to analyse said sample in order to measure a number of parameters according to specific conductivity and potentiometric methodologies as well as to measure the redox potential value of said sample and its temperature; restoring means, apt to calculate, according to the above measured values, the quantity of correction chemicals to be added to the pickling bath in order to restore at the desired level the value of said parameters and to actuate at least a device to add into said pickling bath said quantities of correction chemicals; further characterised in that said measured parameters are the concentrations of sulphuric acid, of hydrofluoric acid and of bivalent and trivalent iron ions.
2. Control device according to claim 1, characterised in that said restoring means introduce into the pickling bath calculated quantities of solutions of said correction chemicals having known concentration.
3. Control device according to claim 2, characterised in that the correction chemicals are sulphuric acid, hydrofluoric acid and an oxidising agent.
4. Control device according to claim 3, characterised in that said oxidising agent is hydrogen peroxide.
5. Control device according to claim 1, characterised in that it comprises at least an analysis device (A).
6. Control device according to claim 5, characterised in that it comprises two analysis devices (A1, A2) simultaneously operating on different parameters.
7. Control device according to claims 1, 3 and 6, characterised in that one of the analysis devices (A1, respectively A2) measures the concentrations in the pickling bath of sulphuric and of hydrofluoric acids and adds sulphuric and hydrofluoric acids to the pickling bath in order to restore relevant given concentration levels, while the other analysis device (A2, respectively A1) measures the concentrations in the pickling bath of the iron ions and adds oxidant agent to the pickling bath to restore the given value of trivalent iron ion concentration and/or the ratio between trivalent and bivalent iron ions.
8. Control device according to claim 7, characterised in that the analysis device (A)

comprises in combination: a sampling module (C) provided with sampling inputs (I) connected in sequence to pickling tanks (V) to send in at least a reservoir placed inside the sampling module (C) a sample of the pickling bath to be analysed; a reagent storage (DR), containing at least the tanks for the reagents utilised for the analyses of said pickling bath sample; dosing means (D) apt to draw from said tanks in the reagent storage (DR) given amounts of chemicals and to transfer the same into analysis vessel (CA); the analysis vessel CA, containing the measure electrodes (EM) utilised to analyse the pickling bath sample, receiving from sampling module (C) the bath sample to be analysed and from dosing means (D) the chemicals necessary for the analysis; a logic unit (UL), controlling and managing the analysis procedures, acquiring and elaborating the information from measure electrodes (EM) and actuating means to send into the pickling bath the solutions containing the correction chemicals.

9. Control device according to claim 8, characterised in that part of the dosing means (D) is apt to draw with low accuracy (from about 2 to about 5%) high quantities of chemicals, and that the remaining dosing means are apt to draw with high accuracy (about 0,1%) small quantities of chemicals.

10. Control device according to claim 9, characterised in that said dosing means (D) having low accuracy and high accuracy are respectively grouped in two different units (D1, D2).

11. Control device according to claim 8, characterised in that it comprises also means to send into analysis vessel (CA) water to rinse the same vessel (CA) and measure electrodes (EM) and to dilute to the desired dilution ratio the pickling bath sample contained into analysis vessel (CA).

12. Control device according to claim 11, characterised in that the rinsing and dilution water has a conductivity lesser than 100 microsiemens.

13. Control device according to claim 8, characterised in that each logic unit (UL) is connected to a central operative post and/or to a logic unit of higher level, by which it can be controlled and managed.

14. Control device according to claim 1, characterised in that said means to perform conductivity measures comprise a conductivity measure cell (CC) provided at one of its extremities with a glass hollow body (B) and having a

substantially cylindrical shape, containing a couple of blackened platinum plaques (EL), at the lower and upper parts of said hollow body (B) being provided holes (F1, F2) letting the sample to be analysed, contained into analysis vessel (CA), to circulate inside the hollow body (B).

5 15. Control device according to claim 14, characterised in that the hollow body (B) has a diameter comprised between 17 and 23 mm and a height comprised between 35 and 45 mm, the (EL) plaques dimensions being between 8 x 12 mm and 3 x 7 mm, the distance from one another being comprised between 12 and 18 mm.

10 16. Control device according to claim 15, characterised in that the hollow body (B) has a diameter of 20 mm and a height of 40 mm, the plaques (EL) dimensions being 10 x 5 mm, the distance from one another being 15 mm.

15 17. Control device according to claim 1, characterised in that said means to perform potentiometric measures comprise a measure electrode (E) immersed into the analysis vessel (CA) and a reference electrode (R) positioned outside the analysis vessel (CA), connected to the solution under measure by a saline bridge constituted by an electrolyte continuously passing through a porous septum (SP) placed at one extremity of a small plastic tube (T).

20 18. Control device according to claim 17, characterised in that the electrolyte contains a product having a viscosity of between 1,15 and 1,45 centipoise at 20 °C.

19. Control device according to claim 18, characterised in that the electrolyte contains glycerine at 10%.

25 20. Control device according to claim 17, characterised in that the measure electrode (E) is constituted by a body in antacid material bearing at one of its extremities a platinum plaque (P) having a mirror finished surface facing downwards.

30 21. Control device according to claims 8, 14 and 17, characterised in that the analysis device (A) also comprises means for chemically washing and water rinsing the analysis vessel (CA), the measure electrode (E) and the porous septum (SP) of the saline bridge, respectively the analysis vessel (CA) and the conductivity measure cell (CC), said means comprising at least slits (F) placed

along the upper edge of the vessel (CA) and a nozzle (U) apt to direct a water flow on the extremity of the measure electrode (E) and on the porous septum (SP), respectively on the conductivity measure cell (CC).

22. Method for controlling nitric acid free pickling baths, characterised in that it comprises at least the following steps:

- taking a sample of a pickling bath;
- measuring the concentration of the acids in said sample of a pickling bath;
- measuring the concentration of the bivalent iron ion in said sample of a pickling bath;
- measuring the concentration of the trivalent iron ion in said sample of a pickling bath;
- measuring the redox potential of said sample of a pickling bath;
- measuring the temperature of said sample of a pickling bath;
- restoring at preset levels the values of said measured concentrations in said pickling bath by adding calculated quantity of correction chemicals to the pickling bath.

23. Method according to claim 22, characterised in that it also comprises the step of measuring the concentration of the free hydrogen peroxide in the baths of finishing/passivation utilised as last operative operation before the final rinsing in the treatment of ferritic and martensitic steels.

24. Method according to claim 22, characterised in that the measure of the concentration in said sample of a pickling bath of the acids comprises at least the following operations:

- filling the analysis vessel (CA), by means of high precision dosing means (D2), with a given water volume having a conductivity of less than 100 microsiemens to obtain a given dilution ratio;
- picking up from a sampling module (C), by means of high precision dosing means (D2), a given volume of the pickling bath sample to be analysed and inserting it into the analysis vessel (CA);
- stirring the solution;
- performing a first conductivity measure (L₁);
- adding into the analysis vessel (CA) a given volume of a solution of ferric

nitrate*9 H₂O;

- stirring of the solution and measuring its temperature (T);
- performing a second conductivity measure (L₂);
- emptying the analysis vessel (CA).

5 25. Method according to claim 24, characterised in that in the analysis vessel (CA) a solution at 750 g/l of ferric nitrate having the same volume than the pickling bath sample to be analysed is added.

26. Method according to claim 24, characterised in that the concentration (as) in said sample of a pickling bath of the sulphuric acid is calculated according to the
10 following equation:

$$as = a \cdot L_1^2 + b \cdot L_1 - c$$

where a, b, c are coefficient of the quadratic equation and L₁ is the result of the first conductivity measure.

27. Method according to claim 24, characterised in that the concentration (af) in
15 said sample of a pickling bath of the hydrofluoric acid is calculated according to the following equation:

$$af = a_1 \cdot \delta^2 + b_1 \cdot \delta - c_1$$

where: a₁, b₁, c₁ are coefficients of the quadratic equation; $\delta = L_2 - L_1 - \phi$; $\phi = c_2 + (c_3 \cdot T)$; L₁ and L₂ are the results of the first and of the second conductivity
20 measure; c₂, c₃ are constants depending on the quantity of ferric nitrate*9 H₂O added into the analysis vessel (CA).

28. Method according to claim 24, characterised in that the determination of the bivalent iron ion concentration in said sample of a pickling bath is performed by means of permanganometric titration.

25 29. Method according to claim 28, characterised in that the determination of the bivalent iron ion concentration in said sample of a pickling bath comprises at least the following operations:

- filling the analysis vessel (CA) with a given water volume to obtain a given dilution ratio;
- 30 • picking up from the sampling module (C), by means of high precision dosing means (D2), a given volume of the pickling bath sample to be analysed, and adding it into the analysis vessel (CA);

- acidifying the diluted pickling bath sample by addition in the analysis vessel (CA), by means of low precision dosing means (D1), of a given non-critical amount of a solution of a strong acid having a known concentration;
- potentiometric titration with a potassium permanganate solution of known concentration added into analysis vessel (CA) by means of high precision dosing means (D2) said potentiometric titration having a present final point or an automatic search of the final point;
- emptying analysis vessel (CA).

30. Method according to claim 22, characterised in that the determination of the trivalent iron ion concentration in said sample of a pickling bath is made by iodometric titration.

31. Method according to claim 30, characterised in that the determination of the trivalent iron ion concentration in said sample of a pickling bath comprises at least the following operations:

- filling the analysis vessel (CA) with a given water volume, to obtain a given dilution ratio;
- picking up from the sampling module (C), by means of high precision dosing means (D2), a given volume of the pickling bath sample to be analysed, and addition of said bath sample into analysis vessel (CA);
- start of stirring;
- adding into analysis vessel (CA), by means of low precision dosing means (D1), a given non-critical volume of a solution, at a known concentration, of a salt of an element which, reacting with sulphuric and hydrofluoric acids, forms soluble salts or easily removable precipitates;
- waiting for a given period of time without stirring;
- adding into analysis vessel (CA), by means of low precision dosing means (D1), a given non-critical volume of a hydrochloric acid solution at known concentration;
- adding into analysis vessel (CA), by means of low precision dosing means (D1), a given non-critical volume of a potassium iodide solution, at known concentration;
- waiting for a given period of time, without stirring;

- stirring the solution;
- potentiometric titration with sodium thiosulphate of known concentration, added by means of high precision dosing means (D2), of the iodine liberated by the reaction of trivalent iron with potassium iodide;

5 • emptying of analysis vessel (CA).

32. Method according to claim 31, characterised in that the salt of an element which, reacting with sulphuric and hydrofluoric acids, forms soluble salts and easily removable precipitates is lanthanum nitrate.

10 33. Method according to claims 29 or 31, characterised in that said volume of water is filled into the analysis vessel (CA) through an overflow tube incorporated into the analysis vessel (CA).

15 34. Method according to claim 22, characterised in that the determination of the redox potential of said sample of a pickling bath is made before the determination of the bivalent iron concentration, in that the thus obtained value of the redox potential is compared with a range of given values and in that if the measured value is outside said range the analysis procedure is stopped and an alarm signal is generated.

35. Method according to claim 23, characterised in that the determination of the free hydrogen peroxide at least comprises the following operations:

- 20 • filling the analysis vessel (CA) with a given water volume to obtain a given dilution ratio;
- picking up from the sampling module (C), by means of high precision dosing means (D2), a given volume of the pickling bath sample to be analysed, and adding it into the analysis vessel (CA);
- 25 • acidifying the diluted pickling bath sample by addition in the analysis vessel (CA), by means of low precision dosing means (D1), of a given non-critical amount of a strong acid of a known concentration;
- potentiometric titration with a potassium permanganate solution of known concentration added into analysis vessel (CA) by means of high precision dosing means (D2) said potentiometric titration having a present final point or
- 30 an automatic search of the final point;
- emptying analysis vessel (CA).

36. Method according to claim 22, characterised in that it also comprises, after each analysis, a water rinsing operation of the analysis vessel (CA), of the means to make potentiometric measures and of the conductivity measure cell; the analysis vessel (CA), the means to make potentiometric measures, the conductivity measure cell and the conductivity measure cell being chemically washed after a given number of analyses.

37. Method according to claim 36, characterised in that said water rinsing comprises at least the following operations:

- fully emptying analysis vessel (CA);
- pouring in said analysis vessel (CA) a large amount of water through slits (F) placed along the upper edge of analysis vessel (CA);
- filling with water said analysis vessel (CA) up to have the tip of said means to make potentiometric measures and the conductivity measure cell immersed;
- emptying analysis vessel (CA);
- further rinsing the tip of said means to make potentiometric measures and the conductivity measure cell, spraying on them some water through a nozzle (U) placed on the analysis vessel (CA);
- emptying analysis vessel (CA) and preparing it for the subsequent analysis.

38. Method according to claims 36 and 37, characterised in that the chemical washing comprises at least the following operations:

- filling with water the analysis vessel (CA) through slits (F) placed around the upper edge of the analysis vessel (CA) up to have the tip of said means to make potentiometric measures and the conductivity measure cell immersed;
- picking up from a tank the amount of the product necessary to obtain the chemical washing solution and sending the latter into said analysis vessel (CA);
- after a given period of time, emptying the analysis vessel (CA) and rinsing it with water to eliminate any trace of the washing chemical solution.

39. Method according to claim 38, characterised in that said chemical washing is made with 10-20% hydrochloric acid.

40. Method according to claim 38, characterised in that the amount of the product necessary to make the chemical washing solution is drawn from a tank placed in

the reagent storage (DR).

41. Method according to claim 22, characterised in that when not working, the analysis vessel (CA) is filled with water through slits (F) placed along the upper edge of the analysis vessel (CA) and through a nozzle (U) placed inside said vessel.

42. Method according to claim 22, characterised in that the concentrations in the pickling bath of the sulphuric acid, of the hydrofluoric acid, of the trivalent iron ions and of the oxidising product are brought back to the desired values by activation of each of the dosing means regulating the addition into the pickling bath of the corresponding correction chemicals for a period of time (s) given by the following formula

$$s = K \cdot (v_0 - v_m) \cdot v_b/p$$

in which:

s = actuating time;

K = factor inversely proportional to the concentration of the correction chemicals;

v_0 = given concentration for the specific correction chemical;

v_m = concentration of said specific correction chemical resulting from the analysis;

V_b = volume of tank;

p = delivery of the addition means.

43. Method according to claim 22, characterised in that the ratio R between the trivalent iron ion and the bivalent iron ion concentrations in the pickling bath is brought back to the desired value by means of the following operations:

- calculating $B_1 = A \cdot R$

in which A is the concentration of the bivalent iron ion resulting from the titration with permanganate, R is the desired ratio between the concentration of, respectively, the trivalent and the bivalent iron ions, and B_1 is the theoretical concentration of the trivalent iron ion;

- comparing B_1 with the measured concentration B of the trivalent iron ion;
- if $B \geq B_1$, do not actuate the dosing means (D2) regulating the input into the pickling bath of an oxidising product;
- if $B < B_1$, activate the dosing means (D2) regulating the input into the pickling bath of an oxidising product for a period of time (s1) expressed by the formula

$$s_1 = K \cdot K_1 \cdot C/p$$

in which:

s_1 = actuating period;

K = factor inversely proportional to the concentration of the corrective chemilas,

K_1 = factor proportional to the tank volume;

$C = (B_1 - B)/R$ = amount of bivalent iron ion to be oxidised to restore the desired value for iron ion concentration;

p = delivery of the addition means.

44. Method according to claims 22, characterised in that the ratio R between the trivalent iron ion and the bivalent iron ion concentrations in the pickling bath is brought back to the desired value by means of the following operations:

- Calculation of the total iron $T = A + B$

where A is the concentration of Fe^{2+} obtained from the permanganometric analysis and B is the concentration of Fe^{3+} obtained from the iodometric analysis.

- Calculation $R = B/A$
- Compare R (present ratio) with R_1 (pre-fixed ratio)
- If $R > R_1$ the logic unit UL does not make any addition of oxidizing product
- If $R < R_1$ the logic unit UL calculates the actuating period s_1 (in seconds) of the addition means regulating the addition the pickling bath of the oxidizing product solution according to the following formula

$$s_1 = K \cdot K_1 \cdot C/p$$

where

$C = A - [(A+B)/(R_1+1)]$ = amount of bivalent iron to oxidize to restore the present ratio R to the prefixed value R_1

s_1 = actuating period (s)

K = coefficient, inversely proportional to the volume of the tank V (l)

P = delivery of the addition means (l/s).

45. Method according to claim 22, characterised in that the logic unit (UL) manages the pickling bath by means of one of the operative procedures loaded into its memory and comprising a plurality of parameters characterising a specific operation and the working parameters of the analysis device to analyse the pickling bath associated to said specific operation.

46. Method according to claim 45, characterised in that each of the operative procedures comprises at least the following information:

- order and kind of analyses to be performed;
- given values for parameters under examination in the pickling bath;
- 5 • magnitude of admissible deviation with respect to said given values, beyond which the logic unit (UL) actuates dosing means (D) to send into the pickling bath the correcting chemicals;
- dilution ratios with water of the pickling bath sample to be analysed.

47. Method according to claim 45, characterised in that the logic unit (UL)
10 performs also an autocalibrating operative procedure activated after a given number of analyses, comprising the steps of:

- picking up from a container a given amount of a solution having known composition (CA) and analysing it;
- transferring said solution to the analysis vessel (CA);
- 15 • comparing the values obtained by the analysis with the expected ones ;
- activate alarms if the deviations between measured values and expected ones are higher than a given amount.

48. Method according to claim 47, characterised in that the solution with known composition is picked up from a container placed in a reagent storage (DR).

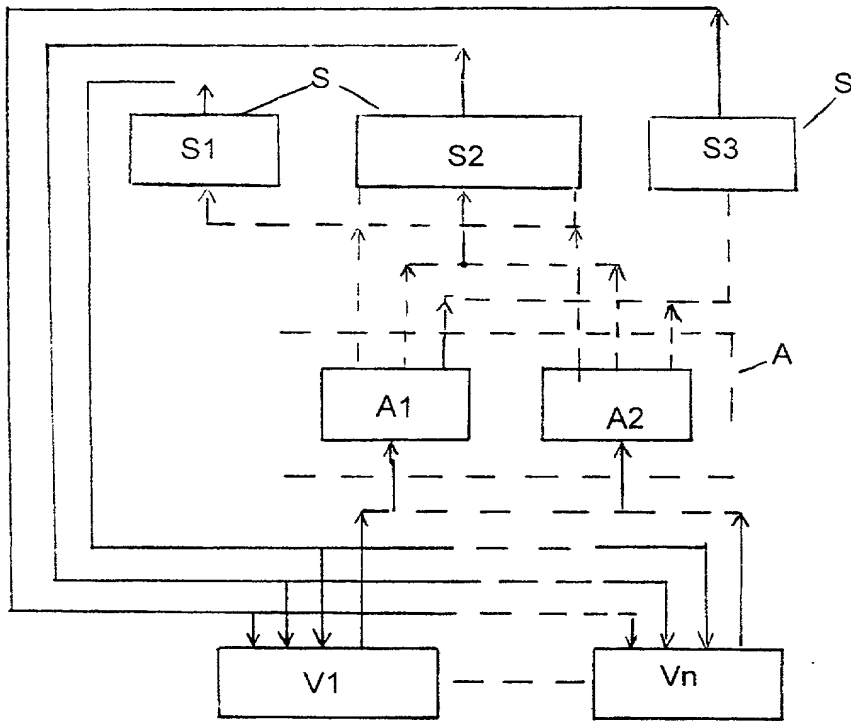


Figure 1

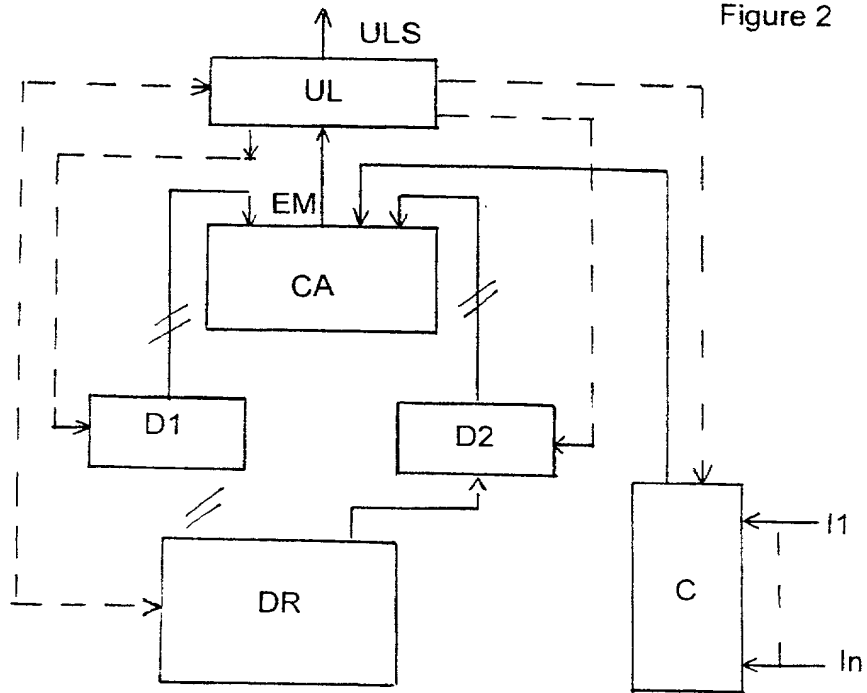


Figure 2

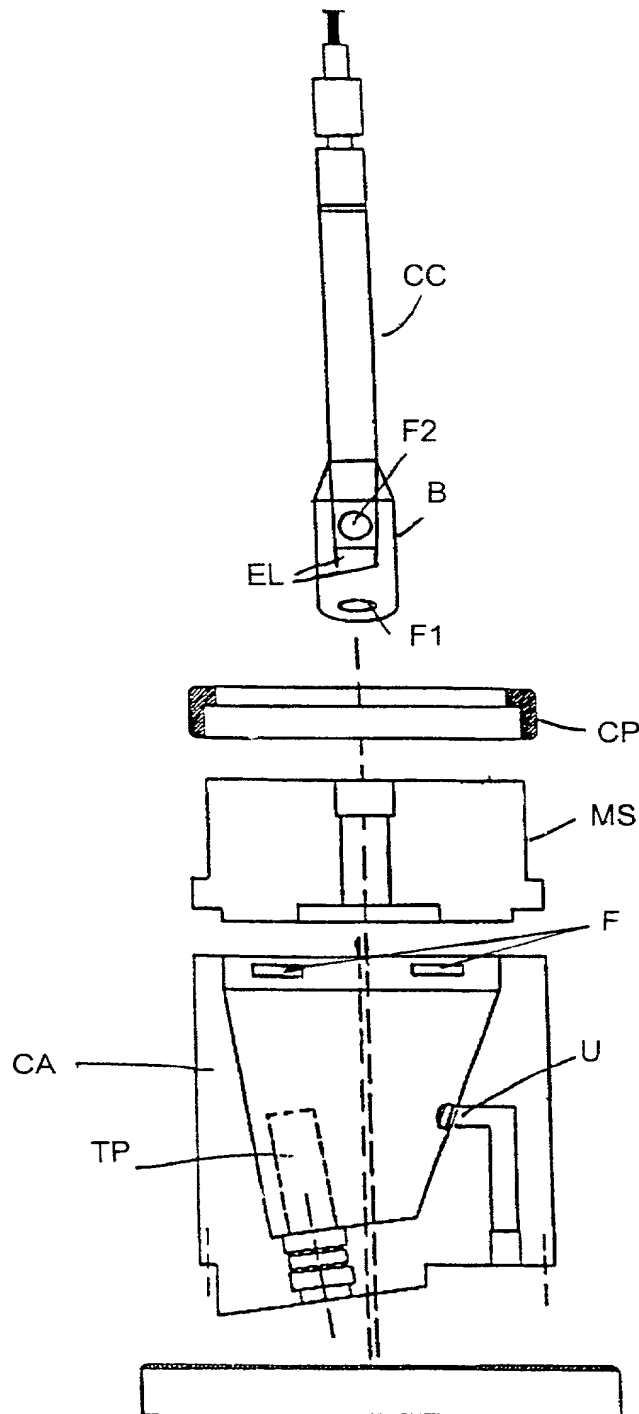


Figure 3

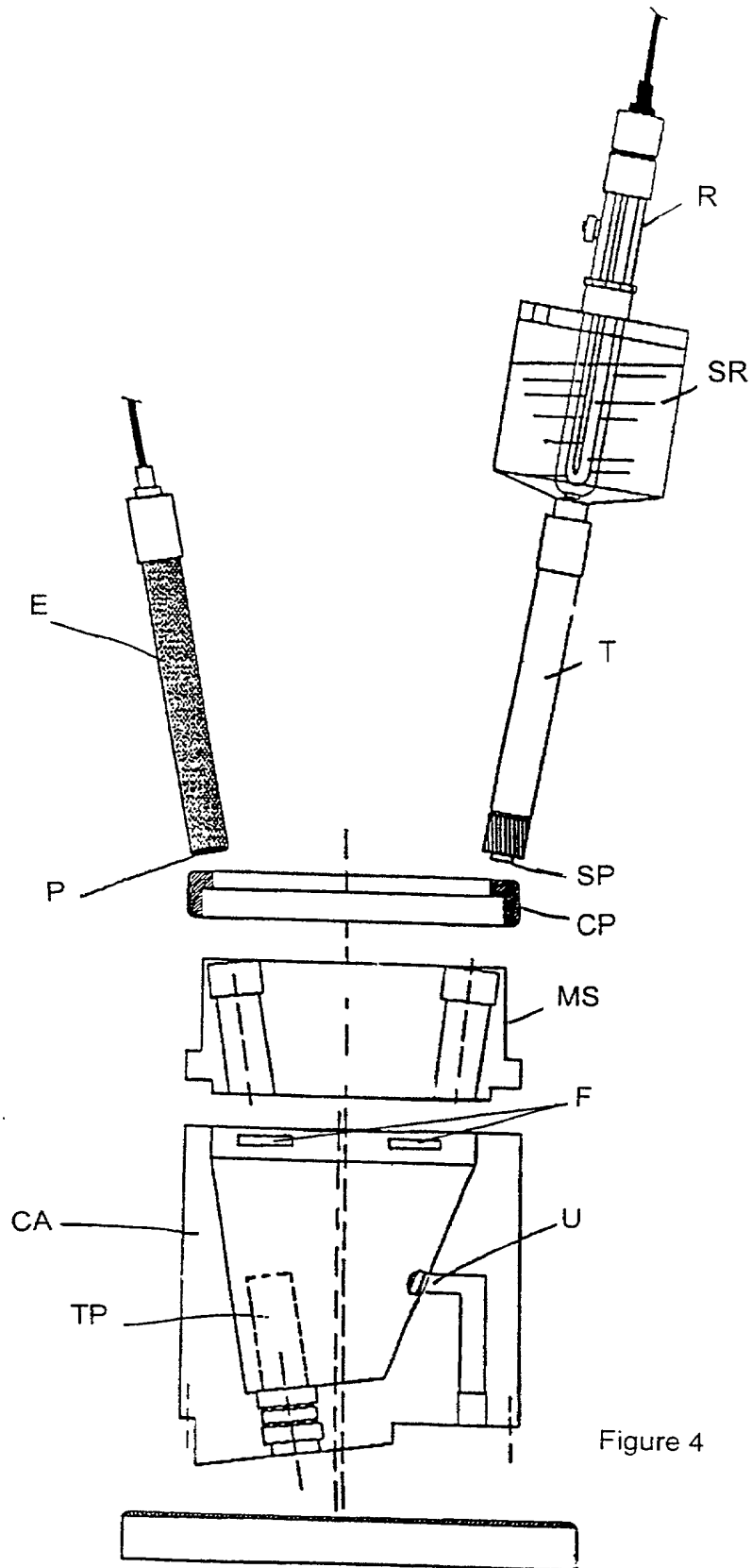


Figure 4

UNITED STATES



UTILITY PATENT APPLICATION DECLARATION AND POWER OF ATTORNEY – ORIGINAL APPLICATION	ATTORNEY'S DOCKET NO.
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I, a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name:

I verily believe I am the original, first and sole inventor (if only one name is listed below) or a joint inventor (if plural inventors are named below) of the invention entitled

(1) TITLE OF INVENTION (1) **DEVICE AND METHOD TO CONTROL STEEL PICKLING PROCESSES**

the specification of which

(2) CHECK APPROPRIATE BOX (2) ☐ is attached hereto.

☒ was filed on 2 December 1999 as Application No. PCT/EP99/09367

and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge my duty to disclose information of which I am aware which is material to the patentability of this application under 37 CFR 1.56(a): the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months prior to this application; and as to applications for patents or inventor's certificate on the invention filed in any country foreign to the United States prior to this application by me or my legal representatives or assigns.

(3) CHECK APPROPRIATE BOX (3) ☐ no such applications have been filed, or

☐ such application(s) have been filed as follows:

EARLIEST FOREIGN APPLICATION(S), IF ANY, FILED WITHIN 12 MONTHS PRIOR TO THIS APPLICATION				
Country	Application Number	Date of Filing (day, month, year)	Date of Issue (day, month, year)	Priority Claimed Under 35 USC 119
(4) ITALY	MI98A002612	2 December 1998		<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
				<input type="checkbox"/> Yes <input type="checkbox"/> No
				<input type="checkbox"/> Yes <input type="checkbox"/> No
ALL FOREIGN APPLICATIONS, IF ANY, FILED MORE THAN 12 MONTHS PRIOR TO THIS APPLICATION				
(4)				

I hereby claim the benefit under Title 35, United States Code § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112. I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

(5) COMPLETE DATA INDICATED IF APPLICABLE (5) _____
 (Application Serial No.) (Filing date) (Status: patented, pending, abandoned)

(5) _____
 (Application Serial No.) (Filing date) (Status: patented, pending, abandoned)

1525 PTUS
1186K

Power of Attorney: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

Jeffrey A. Schwab, Registration Number 24,490
Thomas E. Spath, Registration Number 25,928
Jay S. Cinamon, Registration Number 24,156

Howard R. Jaeger, Registration Number 31,376
Anthony Coppola, Registration Number 41,493

Send correspondence to:
ABELMAN, FRAYNE & SCHWAB
150 East 42nd Street
New York, New York 10017-5612

Direct telephone calls to:
Jeffrey A. Schwab, Thomas E. Spath,
Jay S. Cinamon, Howard R. Jaeger,
or Anthony Coppola at (212) 949-9022

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

(6) DETAILS
REQUIRED
FOR EACH
INVENTOR

Full Name of Sole or First Inventor Paolo GIORDANI	Inventor's Signature <i>Paolo Giordani</i>	Date 13.06.2001
Residence Via Cappuccini 80/A - 26013 CREMA - ITALY	<i>ITX</i>	Citizenship ITALIAN
Post Office Address Via Cappuccini 80/A - 26013 CREMA - ITALY		
Full Name of Second Joint Inventor, If Any Fabio MUSIANI	Inventor's Signature <i>Fabio Musiani</i>	Date 13.06.2001
Residence Via Botte 9 - 48024 MASSALOMBARDA - ITALY	<i>ITX</i>	Citizenship ITALIAN
Post Office Address Via Botte 9 - 48024 MASSALOMBARDA - ITALY		
Full Name of Third Inventor, If Any Ioannis DEMERTZIS	Inventor's Signature <i>Ioannis Demertzis</i>	Date 13.06.2001
Residence Via Cadibona 18 - 20137 MILAN - ITALY	<i>ITX</i>	Citizenship GREEK
Post Office Address Via Cadibona 18 - 20137 MILAN - ITALY		
Full Name of Fourth Joint Inventor, If Any Sandro FORTUNATI	Inventor's Signature <i>Sandro Fortunati</i>	Date 13.06.2001
Residence c/o ACCIAI SPECIALI TERNI S.p.A., Viale B. Brin 218 - 05100 TERNI - ITALY	<i>ITX</i>	Citizenship ITALIAN
Post Office Address c/o ACCIAI SPECIALI TERNI S.p.A., Viale B. Brin 218 - 05100 TERNI - ITALY		
Full Name of Fifth Joint Inventor, If Any Franco MANCIA	Inventor's Signature <i>Franco Mancia</i>	Date 13.06.2001
Residence c/o CENTRO SVILUPPO MATERIALI S.p.A., Via di Castel Romano 100/102, 00129 ROMA, IT	<i>ITX</i>	Citizenship ITALIAN
Post Office Address c/o CENTRO SVILUPPO MATERIALI S.p.A., Via di Castel Romano 100/102, 00129 ROMA, ITALY		
Full Name of Sixth Joint Inventor, If Any Ezio NOVARO	Inventor's Signature <i>Ezio Novaro</i>	Date 13.06.2001
Residence c/o CENTRO SVILUPPO MATERIALI S.p.A., Via di Castel Romano 100/102, 00129 ROMA, IT	<i>ITX</i>	Citizenship ITALIAN
Post Office Address c/o CENTRO SVILUPPO MATERIALI S.p.A., Via di Castel Romano 100/102, 00129 ROMA, ITALY		
Full Name of Seventh Joint Inventor, If Any	Inventor's Signature	Date
Residence		Citizenship
Post Office Address		